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Atmos. Chem. Phys. Discuss., 7, 9203–9233, 2007
www.atmos-chem-phys-discuss.net/7/9203/2007/

Atmospheric Chemistry and Physics Discussions

Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006

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Received: 30 May 2007 – Accepted: 6 June 2007 – Published: 28 June 2007

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Abstract

Fast measurements of aerosol and gas-phase constituents coupled with the ISORROPIA-II thermodynamic equilibrium model are used to study the partitioning of semivolatile inorganic species and phase state of Mexico City aerosol sampled at the T1 site during the MILAGRO 2006 campaign. Overall, predicted semivolatile partitioning agrees well with measurements. $PM_{2.5}$ is insensitive to changes in ammonia but is to acidic semivolatile species. Semi-volatile partitioning equilibrates on a timescale between 6 and 20 min. When the aerosol sulfate-to-nitrate molar ratio is less than 1, predictions improve substantially if the aerosol is assumed to follow the deliquescent phase diagram. Treating crustal species as "equivalent sodium" (rather than explicitly) in the thermodynamic equilibrium calculations introduces important biases in predicted aerosol water uptake, nitrate and ammonium; neglecting crustals further increases errors dramatically. This suggests that explicitly considering crustals in the thermodynamic calculations are required to accurately predict the partitioning and phase state of aerosols.

1 Introduction

Atmospheric particulate matter plays a central role in atmospheric phenomena like visibility reduction, public health, formation of acid rain and climate change. Fine particles, otherwise called $PM_{2.5}$ (particles with diameter less than 2.5 μm) are prime contributors to the above processes, a quantitative understanding of which requires knowledge of their phase and composition. Much of the dry particle mass is inorganic (25–75%) (Heitzenberg, 1989) with the main components often being ammonium (NH_4^+), sulfate (SO_4^{2-}), and nitrate (NO_3^-). Depending on the location, sodium (Na^+) and chloride (Cl^-) may also be found as well as crustal species (Ca^{2+}, K^+, Mg^{2+}) which are associated with dust (Heitzenberg, 1989; Malm et al., 1994). These species may be dissolved in aqueous phase, or in the form of precipitated solids, and some may partially volatilize

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(e.g. NH_4^+, NO_3^-, Cl^-). The partitioning of these species between gas, liquid and solid phase is determined by thermodynamic equilibrium and can be simulated by thermodynamic equilibrium models, such as AIM2 (Wexler and Clegg, 2002), SCAPE2 (Meng et al., 1995), GFEMN (Ansari and Pandis, 1999a,b), UHAERO (Amundson et al., 2006) and ISORROPIA-II (Fountoukis and Nenes, 2007). These models differ in the chemical species that they can treat, the method used to solve for equilibrium composition, the type of input they can accept, and their computational efficiency. Similarities and differences between these models are discussed elsewhere (e.g., Ansari and Pandis, 1999a, b; Zhang et al., 2000; Amundson et al., 2006; Fountoukis and Nenes, 2007).

An important question regarding the partitioning of semivolatile inorganic aerosol phase is whether the assumption of thermodynamic equilibrium is adequate to predict chemical composition. A key factor is aerosol size (Wexler and Seinfeld 1991, 1992; Meng and Seinfeld, 1996; Dassios and Pandis, 1999; Cruz et al., 2000); for submicron particles, equilibrium is achieved typically within a few minutes, often faster than the timescale of ambient condition change (Meng and Seinfeld, 1996; Dassios and Pandis, 1999; Cruz et al., 2000) so that the assumption of instantaneous equilibrium can be used to model composition. Coarse mode particles however require substantial time, on the order of an hour or more (Meng and Seinfeld, 1996; Dassios and Pandis, 1999; Cruz et al., 2000), so explicit condensation/evaporation dynamics is required for modeling composition (e.g., Pilinis et al., 2000; Capaldo et al., 2000).

Several studies have been conducted to test the applicability of the equilibrium assumption by comparing thermodynamic model predictions against observational data. Moya et al. (2001) used ISORROPIA, SCAPE2 and GFEMN to study the partitioning of nitrate and ammonium in Mexico City during the 1997 IMADA-AVER field campaign. Using daily and 6-h average $PM_{2.5}$ data, Moya et al. (2001) found the equilibrium approach reproduced most of the data, however a few discrepancies were found and were attributed to the implicit treatment of crustal species (treated as "equivalent" sodium by ISORROPIA and GFEMN) as opposed to the explicit treatment (by SCAPE2) and to the use of IMADA observations averaged over long periods of time (6 h). Zhang et

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al. (2003) assessed the nitrate – ammonium equilibrium assumption using the ISORROPIA model and high resolution (5-min average) data obtained during the 1999 Atlanta Supersite Experiment. They found good agreement for nitrate and ammonium when a 15% correction (within measurement uncertainty) in $PM_{2.5}$ SO_4^{2-} was applied. Takahama et al. (2004) used GFEMN to model the partitioning of nitrate during the 2001–2002 Pittsburg Air Quality Study (PAQS). Using 1 and 2-h average measurements of $PM_{2.5}$ they found most of the predictions of nitrate to agree with observations to within experimental uncertainty. Yu et al. (2005) used the 1999 Atlanta Supersite Experiment data, the PAQS dataset, and 12-h measurement data from North Carolina in 1999 to assess the ability of the three-dimensional (3-D) Community Multiscale Air Quality (CMAQ) model (which includes ISORROPIA) to predict aerosol nitrate. They found that errors associated with sulfate and total ammonium predictions of the 3-D model can lead to large errors in predicted aerosol nitrate. Metzger et al. (2006) used ISORROPIA, SCAPE2 and EQSAM2 to study the partitioning of ammonium and nitrate during the Mediterranean INtensive Oxidant Study (MINOS) experiment. Using 2 and 3-h average measurements they showed that only when crustal species and (lumped) organic acids are explicitly accounted for, the observed gas – aerosol partitioning of ammonia and nitric acid can be accurately reproduced. Using CMAQ and ISORROPIA, Nowak et al. (2006) analyzed gas phase ammonia measurements (using a PILS for the aerosol and a CIMS instrument for the gas phase data) from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE) and found excellent agreement for NH_3 and NH_4^+ concentrations.

The phase state of aerosols is another important issue in aerosol modeling, as they can follow the deliquescence branch (in which solids precipitate out of the aqueous aerosol phase upon saturation) or the efflorescence branch (in which the aerosol is always an aqueous phase and solids are not allowed to form). Phase state may depend on RH history. For example, as RH increases, particles deliquesce, while when RH decreases, particle may not crystallize at its initial deliquescence point, but retain water until a much lower relative humidity (hysteresis phenomenon). Ansari and Pan-

dis (2000) studied the impact of assuming a deliquescent vs. effluorescent path on the partitioning of nitrate in Southern California; when nitrate concentrations were low ($<8\,\mu g\,m^{-3}$), the consideration of both branches of aerosol behavior is essential, while no significant difference between stable and metastable predictions was found for high ($>8\,\mu g\,m^{-3}$) aerosol nitrate concentrations. Moya et al. (2002) showed that the assumption of metastable state for sub-micrometer particles may introduce large errors when RH <60% highlighting the importance of deliquescence predictions at low RH.

Most studies to date either use measurements averaged over long times or use models that do not explicitly treat crustals. If measurements are slow, significant variations in T, RH and aerosol precursor concentrations may occur during sampling which cannot be accounted for in equilibrium calculations. Additionally, the consideration of crustal material in predicting the partitioning of nitrate and ammonium, especially in areas where dust comprises a significant portion of total PM, can considerably affect the aerosol thermodynamics and improve model predictions (Ansari and Pandis, 1999; Moya et al., 2002).

In the present work, we use ISORROPIA-II, which treats the thermodynamics of the K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-HSO_4^--NO_3^--Cl^--H_2O aerosol system, to a) test the thermodynamic equilibrium assumption for the Mexico City environment during the MILAGRO 2006 campaign, b) gain insight on the preferred phase behavior of the aerosol (i.e. deliquescent or metastable), and, c) assess the importance of a full thermodynamic treatment versus neglecting the presence of crustals (or treating them as equivalent sodium). The MILAGRO 2006 dataset analyzed here is ideal for the objectives of this study, because of significant concentrations of all the inorganic species mentioned above.

2 Observational data

The Megacity Initiative: Local and Global Research Observations (MILAGRO) Campaign took place in 1–30 March 2006 (http://www.eol.ucar.edu/projects/milagro/). The

three main ground locations were: one site at the Instituto Mexicano del Petróleo (T0 site, latitude: 19.25 N, longitude: 99.10 W), another at the Universidad Tecnológica de Tecámac in the State of Mexico (T1 site, latitude: 19.703 N, longitude: 98.982 W) and a third in Rancho La Bisnaga in the State of Hidalgo (T2 site, latitude: 20.01 N, longitude: 98.909 W). The data analyzed in this study were collected at the T1 site from 21 to 30 March 2006 and include fine particulate matter concentrations ($PM_{2.5}$) of NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Cl^-, Ca^{2+}, K^+, Mg^{2+}, gas phase concentrations of NH_3, HNO_3, HCl and ambient temperature, and relative humidity.

The $PM_{2.5}$ ion concentrations were measured by a Particle Into Liquid Sampler (PILS) with a 6-min integrated sampling period and a new chromatogram being started every 17 min (Orsini et al., 2003). The advantage of this instrument is the simultaneous measurements of important inorganic anions and cations at high time-resolution. $NH_{3(g)}$ concentrations were obtained every minute with quantum-cascade laser (QCL) spectrometer (Fischer et al., 2007[1]), while volatile nitrate (i.e. $HNO_{3(g)}$ + NH_4NO_3) concentrations were measured every 5 min by a thermal dissociation-laser induced fluorescence of nitrogen oxides (TD-LIF, Day et al., 2002; Farmer et al., 2006). Ambient temperature (T), pressure and relative humidity (RH) data are based on the measurements of the Vaisala Y50 Sensor which was operated with a 1-min time resolution. Aerosol particles ($PM_{2.5}$) were also collected (6-hour samples) with a cascade micro-orifice uniform deposit impactor (MOUDI) (MSP Model 100, Marple et al., 1991) at the same site and sampling period.

6-minute averages of $NH_{3(g)}$ concentrations, T and RH were obtained to correspond to the 5-min averages of $HNO_{3(g)}$ and 6-min averages of $PM_{2.5}$ ion concentrations. In ~26% of the cases, the 5-min averages of $HNO_{3(g)}$ data were not coincident with the 6-min PILS concentrations, therefore a ~20-min average were considered instead

[1]Fischer, M. L., VanReken, T. M., Coffey, M. T., Wood, E., Herndon, S. C., Littlejohn, D., and Hannigan, J. W.: Measurements of ammonia at the T1 site during MILAGRO 2006, in review, 2007.

(average of two measurements with a 10-min interval between the two data points). The TD-LIF measurement is the sum of gas-phase and semivolatile nitrate (i.e. $HNO_{3(g)}$ + NH_4NO_3), from which $HNO_{3(g)}$ is obtained by subtracting $PM_{2.5}$ ammonium nitrate concentrations from the PILS; this can be done because preliminary ISORROPIA-II calculations suggest that the PILS nitrate is entirely semivolatile (i.e. NH_4NO_3 only). Aerosol K^+ was not accurately measured by PILS due to a calibration interference; instead, it was estimated based on a nearly constant ratio (~0.4) of K^+ to the sum of crustal species (Ca^{2+}, K^+, Mg^{2+}) obtained from the impactor data for the same site and sampling period. Gas-phase hydrochloric acid ($HCl_{(g)}$) concentrations were assumed to be zero (hence total Cl^- was equal to aerosol Cl^-). The validity of this assumption is assessed in Sect. 4. The measurement uncertainty was estimated to be approximately ±20% for the PILS instrument (Orsini et al., 2003), ±10% for the $NH_{3(g)}$ measurement (Fischer et al., 2007[1]), ±30% for the TD-LIF instrument (Day et al., 2002; Farmer et al., 2006) and ±5% for *T* and RH. The $HNO_{3(g)}$ uncertainty, $\sigma_{HNO_{3(g)}}$, was estimated from the uncertainties of volatile $\sigma_{(TD-LIF\ nitrate)}$, and PILS nitrate $\sigma_{(PILS\ nitrate)}$, respectively, as:

$$\sigma^2_{HNO_{3(g)}} = \sigma^2_{(TD-LIF\ nitrate)} + \sigma^2_{(PILS\ nitrate)} \quad (1)$$

The reported detection limit for the PILS concentrations is 0.02 $\mu g\,m^{-3}$ for PILS Na^+, NH_4^+, NO_3^- and SO_4^{2-}, 0.002 $\mu g\,m^{-3}$ for PILS Ca^{2+}, Mg^{2+} and Cl^- and 0.35 $\mu g\,m^{-3}$ for the QCL $NH_{3(g)}$ measurement.

Overall, 102 6-min data points were obtained for which measurements of all particulate and gaseous species are available. Ammonia was predominantly in the gas phase while nitrate was dominant in the aerosol phase. The total (gas + particulate) ammonia (TA) to sulfate molar ratio was much larger than 2 (average value = 26.5) indicating sulfate poor aerosols. Relatively low concentrations of Na^+ (0.063±0.113 $\mu g\,m^{-3}$), Ca^{2+}(0.116±0.206 $\mu g\,m^{-3}$), K^+ (0.097±0.140 $\mu g\,m^{-3}$) and Mg^{2+} (0.033±0.051 $\mu g\,m^{-3}$) were detected while the total $PM_{2.5}$ mass was, on average,

28.47±13.03 $\mu g\,m^{-3}$. Temperature did not vary significantly over the measurement period of study (mean value of 289.5±5.1 K) while RH varied significantly (mean value of 58.1±22.6%), exhibiting a typical diurnal cycle which peaks in the evening and early morning and is minimum at around noon. Fig. 1 shows an example of diurnal profiles of measured ammonium, nitrate and ambient RH for March 27. A detailed overview of the dataset and meteorological conditions is given elsewhere (e.g. Doran et al., 2007; Fast et al., 2007).

3 Aerosol equilibrium modeling

ISORROPIA-II (Fountoukis and Nenes, 2007) is a computationally efficient code that treats the thermodynamics of K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosol systems and is used in this study. ISORROPIA-II is designed to solve two classes of problems: (a) forward (or "closed") problems, in which known quantities are T, RH and the total (gas + aerosol) concentrations of NH_3, H_2SO_4, Na, HCl, HNO_3, Ca, K, and Mg, and, (b) reverse (or "open") problems, in which known quantities are T, RH and the concentrations of aerosol NH_4, SO_4, Na, Cl, NO_3, Ca, K, and Mg. The output of both problems is the concentration of species in gas and aerosol (solid/liquid) phase. ISORROPIA-II can predict composition for the "stable" (or deliquescent path) solution where salts precipitate once the aqueous phase becomes saturated with respect to a salt, and, a "metastable" (efflorescent path) solution, in which the aerosol is composed only of an aqueous phase regardless of its saturation state. For the dataset of this study, the forward mode of ISORROPIA-II is used.

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4 Results and discussion

4.1 Model vs. observations

In this section we evaluate the ability of ISORROPIA-II to reproduce the observed partitioning of ammonia, nitrate and chloride, which will test the expectation that equilibrium partitioning of semivolatile aerosol species is attained somewhere between 6 and 30 min. Figures 2a–e show predicted vs. observed concentrations of gas-phase ammonia ($NH_{3(g)}$), nitric acid ($HNO_{3(g)}$), aerosol phase ammonium ($NH_{4(p)}$), nitrate ($NO_{3(p)}$) and chloride ($Cl_{(p)}$), respectively; Table 1 summarizes the corresponding error metrics. For the simulations of Fig. 2, ISORROPIA-II was run in forward mode and stable state conditions. Most of the total ammonia (88.7% on average) resides in the gas phase. The data have been separated into 4 classes based on a "completeness factor" (CF). For half of the data analyzed (51%), 6-min average measurements of all (gas + particulate phase) species were available; these data are represented as "CF=0". For ~26% of the data, only 20-min average measurement of ion concentrations from the PILS instrument were available and are "CF=1" data. Subtracting the PILS ammonium nitrate measurement from the TD-LIF (i.e. $HNO_{3(g)}$ + NH_4NO_3) occasionally resulted in a negative $HNO_{3(g)}$. Under such conditions, $HNO_{3(g)}$ is assumed zero, and the data is indicated as "CF=2" if they correspond to 6-minute averages (13% of the data), and "CF=3" for 20 min averages (10% of the data). The prediction skill of ISORROPIA is quantifed in terms of two error metrics, the normalized mean error (NME), $\mathrm{NME}=\frac{\sum_i^n |I_i - O_i|}{\sum_i^n O_i}$, and normalized mean bias (NMB), $\mathrm{NMB}=\frac{\sum_i^n (I_i - O_i)}{\sum_i^n O_i}$, where I_i represents predictions of ISORROPIA-II for data point i, O_i represents observations and n is the total number of data points. NME gives an estimation of the overall discrepancy (scatter) between predictions and observations, while NMB is sensitive to systematic errors (biases).

A very good agreement between model predictions and observations was found for

$NH_{3(g)}$ (Fig. 2a) with a NME of 5.3%, a slope of 0.991, an intercept of –0.676 $\mu g\,m^{-3}$ (much smaller than concentrations of $NH_{3(g)}$) and an R^2 of 0.992. This is not surprising, as most of the ammonia resides in the gas phase, so $NH_{3(g)}$ is insensitive to prediction errors. Particulate ammonium (Fig. 2b) was systematically overpredicted, as shown by the 37.1% NMB (Table 1). This overprediction could arise from the phase state assumption, departure from equilibrium or measurement uncertainty; all of these possibilities are explored in Sect. 4.3.

Predictions of $HNO_{3(g)}$ were subject to significant scatter (Fig. 2c), with a NME of 80.8% but the bias was comparable to the other species (Table 1). The scatter is attributed to a) the fact that particles in the PM_{10} - $PM_{2.5}$ range are not included in our calculations (although too large to be in equilibrium with the gas phase, they could still react with nitric acid and introduce some prediction error), b) zero concentrations of $HNO_{3(g)}$ for a portion of the data (CF=2 and 3), and, c) low, on average, concentrations of gas phase nitrate which results in predictions of $HNO_{3(g)}$ being very sensitive to errors in particulate nitrate ($NO_{3(p)}$). When partitioning is predominantly in one phase, small errors in its predicted concentration are substantially amplified in the other phase. Additionally, the estimated uncertainty for $HNO_{3(g)}$ (using Eq. 1) was found to be roughly ~100%; the agreement between predicted and observed $HNO_{3(g)}$ is in fact within the estimated uncertainty. For particulate nitrate (Fig. 2d), ISORROPIA-II predictions agree well with observations with a NME of 27.2% and a small bias (NMB = 8.0%).

Observed concentrations of Cl^- agree well (NME=15.5%) with predicted values (Fig. 2e); ISORROPIA-II predicts very small amounts of chloride in the gas phase because the large excess of $NH_{3(g)}$ tends to drive Cl^- almost completely into the aerosol phase. This justifies (to first order) the assumption of zero $HCl_{(g)}$ in the thermodynamic calculations. However, the NME and NMB are almost identical in magnitude; this suggests that the prediction error is likely only from the "missing" (small) amount of $HCl_{(g)}$ that are not considered in the calculations of Fig. 2e. Minimizing the NMB would require on average 0.03 $\mu g\,m^{-3}$ gas-phase HCl (min:0, max: 0.3 $\mu g\,m^{-3}$), which

is consistent with the sub-ppb estimates of $HCl_{(g)}$ by San Martini et al. (2006) for Mexico City aerosol during MCMA-2003 and with measurements (∼1 ppb) reported by Moya et al. (2004).

Agreement between predictions and measurements depends on many factors, such as equilibrium timescale and measurement uncertainty; we assess the importance of each by examining the prediction skill between CF classes, since a) the averaging timescale changes, and, b) the calculated zero concentration of $HNO_{3(g)}$ for some of the data may lead to a biased prediction. Figure 2 (and Table 1) shows that the closure for CF=0 data is slightly worse than for CF=1 to 3, which suggests that the averaging timescale affects the bias. Since the NMB and NME for particulate nitrate are consistent between CF classifications, this suggests that the TD-LIF provides an excellent measure of volatile nitrate. Based on work to date (e.g., Meng and Seinfeld, 1996; Dassios and Pandis, 1999; Cruz et al., 2000) we expect the equilibration timescale to be ∼10 min; indeed the Table 1 results support this, as NMB is consistently minimum for the 20 min data (Table 1). To further explore that the decrease in NMB is a result of equilibration timescale (and not any other experimental uncertainty), we use the CF=0 data, compute 35 min averages and compare against the thermodynamic predictions. Table 2 shows results of calculations using ∼20 min (CF=1) and ∼35 min; the latter was computed by averaging consecutive 6-min (i.e., CF=0) measurements. As can be seen, NME and NMB decreases between the 6 and 20 min averages, but increases notably for the 35 min averages suggesting that the timescale of equilibrium indeed ranges between 6 and 20 min.

Although NMB strongly depends on the averaging time, NME does not. This may be the residual effect of particles in the $PM_{10} - PM_{2.5}$ reacting with nitrates; since coarse particles vary significantly throughout the dataset and are not included in our calculations, their effect likely manifests as "scatter" in the predictions. This suggests that up to 30% of the unresolved particulate nitrate (which is expressed as ∼30% NME) is associated with particles in the $PM_{10} - PM_{2.5}$ range.

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4.2 Deliquescence vs. efflorescence

Due to the hysteresis effect, there is always an issue on what is the appropriate thermodynamic state assumption for RH <60%, where aerosols can often form a solid phase of precipitated salts (Ansari and Pandis, 2000; Moya et al., 2002). This dataset covers a wide range of RH (19–94%) and makes it possible to assess the preferred phase transition path (i.e. deliquescence or efflorescence branch) for Mexico City aerosol.

In Fig. 3 we plot the stable (deliquescence) and metastable (efflorescence) solution predictions of ISORROPIA-II compared to observations for $NH_{4(p)}$ and $NO_{3(p)}$ as a function of RH. The stable state solution of ISORROPIA-II predicts higher concentrations of aerosol ammonium and aerosol nitrate at RH <50% (which is a typical deliquescence point for the salt mixtures under consideration). This is in agreement with previous studies (Ansari and Pandis, 2000) and is primarily attributed to high concentrations of ammonium nitrate formed in the stable state solution of ISORROPIA II through the reaction $NH_{3(g)} + HNO_3(g) \leftrightarrow NH_4NO_{3(s)}$. At low RH (<50%), the stable state solution predicts a solid phase consisting mainly of $(NH_4)_2SO_4$ and NH_4NO_3. The metastable state solution assumes the particulates are composed of an aqueous supersaturated solution throughout the whole RH regime; hence no solid NH_4NO_3 is allowed to form. For RH <50%, the metastable solution predicts less $NO_{3(p)}$ and $NH_{4(p)}$ as compared to the stable solution. At higher RH, solid NH_4NO_3 dissolves and both "stable" and "metastable" aerosol predictions become identical.

The difference between stable and metastable solutions predictions shown in Fig. 3 are quantified in Table 3; NME and NMB are computed only for data with RH<50%. For aerosol ammonium, although the NME for the two solutions of ISORROPIA II is essentially the same, the opposite sign in NMB (Table 3), indicates an overprediction (+11%) of ammonium by the stable state and an underprediction (–9%) by the metastable solution. The systematic overprediction of ammonium by the stable solution (seen in Fig. 2) may partially reflect measurement uncertainty, which is analyzed in detail in Sect. 4.3. For aerosol nitrate, the error and bias between predictions and observations is sig-

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nificantly larger when using the metastable solution (NME=47.4%, NMB=–46.4%) of ISORROPIA II compared to the stable state solution (NME=25.8%, NMB=–18.5%) for RH <50%, suggesting that aerosols in Mexico City prefer the deliquescence branch of the phase diagram. However, Moya et al. (2007)[2] showed that the efflorescence branch gives better agreement between predictions and observations at low RH during the MER 2005 campaign (Mexico City downtown). An important difference between the two datasets is the sulfate-to-nitrate (SO_4^{2-}/NO_3^-) molar ratio, being larger than unity for the MER data and less than unity for the current dataset (on average $SO_4^{2-}/NO_3^- \approx 0.7$). Since a subset of the current dataset exhibited a SO_4^{2-}/NO_3^- larger than 1, we examine the possibility that particulate SO_4^{2-}/NO_3^- correlates with a change in the preferred phase state for RH below 50%. In Table 4 we show the performance of both stable and metastable solution of ISORROPIA-II at RH below 50% and for aerosol SO_4^{2-}/NO_3^- ratio larger and less than 1. At aerosol $SO_4^{2-}/NO_3^- < 1$, NME and NMB are much larger in the metastable solution for $HNO_{3(g)}$ and $NO_{3(p)}$ and slightly larger for $NH_{3(g)}$ and $NH_{4(p)}$ while for aerosol $SO_4^{2-}/NO_3^- > 1$ the opposite is seen (although with much smaller differences in NMB between the two solutions). The results of this study, combined with Moya et al. (2007)[2] suggest that the stable state is preferred when $SO_4^{2-}/NO_3^- < 1$ and vice versa.

4.3 Sensitivity of model predictions to aerosol precursor concentrations

In this section we explore the sensitivity of predictions to aerosol precursor concentrations to a) assess the importance of measurement uncertainty on predictions, and, b) assess the sensitivity of $PM_{2.5}$ to changes in emitted precursors. The sensitivity is assessed by perturbing the input concentrations of total ammonia (TA), total nitrate (TN),

[2]Moya, M., Fountoukis, C., Nenes, A., Matías, E., and Grutter, M.: Predicting diurnal variability of fine inorganic aerosols and their gas-phase precursors during February 2005 near downtown Mexico City: SCAPE2 and ISORROPIA-II model simulations, in review, 2007.

total sulfate (TS), crustals and sodium by ±20% (approximately the PILS measurement uncertainty). The results of this analysis are shown in Table 5. A 20% increase in TS does not improve the agreement between predictions and observations; in fact, a slight increase of the NME was found for ammonia and nitrate. Since the impactor data showed ~40% (on average) higher TS than the PILS (not shown), we further perturb TS by 40%, but NME does not decrease (67.9% for $NH_{4(p)}$ and 27.8% for $NO_{3(p)}$). A +20% perturbation in crustals and sodium concentrations however, slightly improved predictions of $NH_{3(g)}$ and $NH_{4(p)}$ and decreased the observed overprediction seen in Fig. 2b; this is because crustals and sodium preferentially neutralize sulfates, so less ammonia binds to form $(NH_4)_2SO_4$ which decreases the predicted $NH_{4(p)}$concentration and increases the amount of $NH_{3(g)}$. In fact, the impactor data suggest that Ca^{2+}, Mg^{2+} and Na^{+} are much higher (approximately 4 times) than obtained with the PILS. Increasing crustals and sodium by a factor of 4 significantly decreases the systematic error between predictions and measurements for particulate ammonium (NMB = 13.6%); predictions for $NH_{3(g)}$ (mean predicted value = 17.42 $\mu g\,m^{-3}$) and $NH_{4(p)}$ (mean predicted value = 2.55 $\mu g\,m^{-3}$) are improved. This implies that the PILS in this dataset may not account for all the crustals present in $PM_{2.5}$.

In Fig. 4 we plot the predicted change (%) in $PM_{2.5}$ nitrate as a function of RH when a 20% decrease in input concentrations of TA, TS and TN is applied. The nitrate response to sulfate is negligible, Δx=0.36%, (Fig. 3, Table 5) because TA concentrations are substantially in excess, and, thus a 20% change in TS is not enough to affect the formation of ammonium nitrate. (In an ammonia-limited environment, a reduction in sulfate would increase aerosol nitrate as ammonia is freed and allowed to react with nitric acid). As seen in Fig. 4, nitrate predictions are sensitive to changes in TA only for RH <60%. This is expected since below the deliquescence point of NH_4NO_3 the partitioning of nitrate is strongly dependent on the ammonia vapor pressure and thus reducing TA reduces the amount of NH_4NO_3 formed. At RH >60%, nitrate is mostly dissolved and unaffected by the changes in TA. Aerosol nitrate predictions are more directly influenced by reductions in TN as shown in Fig. 4 and Table 5 (Δx=–22.8%),

and is in agreement with Takahama et al. (2004). The sensitivity of aerosol nitrate is RH-dependent as the partitioning of nitrate strongly depends on the amount of aerosol water.

4.4 Importance of explicitly treating crustal species

Often thermodynamic models treat the presence of crustals as mole-equivalent sodium (i.e. $Ca^{2+} = 2Na^{+}$, $Mg^{2+} = 2Na^{+}$, $K^{+} = Na^{+}$) or as insoluble. In this section we examine the impact of these assumptions, versus using full thermodynamics. Table 6 displays a summary of this sensitivity test; shown are average concentrations and error metrics for nitrate, ammonium and water with ISORROPIA-II. For all the simulations we used the concentrations of crustals and sodium from the impactor data. When Ca^{2+}, K^{+} and Mg^{2+} are treated as insoluble (unreactive), ISORROPIA-II predicts higher, on average, concentrations of ammonium compared to both the equivalent-Na and explicit treatment, since more sulfate is available to bind with ammonium, and thus the error and bias between predicted and observed ammonium increases for the insoluble approach (Table 6). For particulate nitrate, NME is the lowest when crustals are treated explicitly. The changes in NME and NMB among the three crustal treatment approaches are rather small since ammonia is enough to fully neutralize the available nitrate regardless of the treatment of crustals. The difference in nitrate prediction when treating crustals explicitly vs. as equivalent sodium is expected to be large in environments where non-volatile nitrate ($Ca(NO_3)_2$, $Mg(NO_3)_2$, KNO_3) is present in significant amounts (Moya et al., 2002; Jacobson, 1999). In the current dataset, aerosol nitrate is present in the form of ammonium nitrate (due to ammonia-rich environment) and thus replacing crustals with sodium is expected to have a minor effect on predicted nitrate response, primarily from differences in predicted water uptake (Table 6). The equivalent Na approach predicts aerosol water content which is higher (by 13.5%) than the one predicted by the explicit treatment of crustals and very close to the insoluble approach (Table 6). This is attributed to the formation of salts with low solubility (e.g., $CaSO_4$) which do not significantly contribute to water uptake. The difference in water content also affects

aerosol acidity (i.e. pH) and water-soluble species concentration. It should be noted that the differences described in Table 6 between the equivalent Na and explicit treatment of crustals are the minimum expected considering the large amounts of ammonia in Mexico City which minimizes the effect of replacing crustals with sodium.

5 Conclusions

This study focuses on thermodynamical modeling of gas-aerosol partitioning sampled during the MILAGRO 2006 campaign in Mexico City. Observations include using high-time resolution measurements of $NH_{3(g)}$, volatile nitrate (i.e. $HNO_{3(g)}$ + NH_4NO_3), NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Cl^-, Ca^{2+}, K^+ and Mg^{2+}. Thermodynamic modeling was done using a state-of-the-art aerosol equilibrium model, ISORROPIA-II (Fountoukis and Nenes, 2007).

In agreement with observations, ISORROPIA-II predicts that ammonia (82.4±10.1%) primarily resides in the gas phase, while most of total nitrate (79.8 ± 25.5%) and chloride (75.3±29.1%) resides in the aerosol phase. The mean observed value for $NH_{3(g)}$ was 17.73 $\mu g\,m^{-3}$ and 5.37 $\mu g\,m^{-3}$ for $NO_{3(p)}$. An excellent agreement between predicted and observed concentration of $NH_{3(g)}$ was found with a NME of 5.3%. Very good agreement was also found for $NO_{3(p)}$ (NME=27.2%), $NH_{4(p)}$ (NME=37.1%) and $Cl_{(p)}$ (NME=15.5%) concentrations for most of the data. Larger discrepancies were seen in predicted $HNO_{3(g)}$ since uncertainties in the volatile nitrate measurement ($HNO_{3(g)}$ + NH_4NO_3) are magnified by the high sensitivity of $HNO_{3(g)}$ because nitrate partitioned primarily to the aerosol phase. A number of important conclusions arise from this study:

1. Application of ISORROPIA-II is largely successful suggesting that the assumption of thermodynamic equilibrium can be appropriate for complex Mexico City aerosols.

2. The timescale for reaching thermodynamic equilibrium for the conditions of aerosol load and ambient temperature ranges between 6 and 20 min.

3. The scatter in nitrate prediction error (~30%) was mostly attributed to reaction of particles between 2.5 and 10 μm diameter with nitrate (the effect of which is not considered in our analysis). This suggests that, on average, up to 30% of the total aerosol nitrate can be associated with $PM_{2.5} - PM_{10}$ particles.

4. At low RH (<50%), the stable state (i.e. deliquescence branch) solution of ISORROPIA-II predicted significantly higher concentrations of aerosol nitrate compared to the metastable (i.e. efflorescence) solution. Further analysis suggests this to be true when at $SO_4^{2-}/NO_3^-<1$. The opposite was seen (although with a much smaller difference between metastable and stable predictions) when $SO_4^{2-}/NO_3^->1$. This can serve as an important constraint for three dimensional air quality models that simulate ambient particle concentrations under conditions characteristic of Mexico City.

5. The volatile fraction of $PM_{2.5}$ was found to be mostly sensitive to changes in TN. This suggests that in an ammonia-rich environment, (such as Mexico City) a combined reduction in TS and TN (rather than TA) appears to be most effective in reducing $PM_{2.5}$ (on a mol per mol basis).

6. Treating crustal species as "equivalent sodium" (or insoluble) has an important impact on predicted aerosol water uptake, nitrate and ammonium, despite the ammonia-rich environment of Mexico City. This suggests that explicit treatment of crustals (when present) is required for accurate predictions of aerosol partitioning and phase state.

7. Concentrations of gas phase HCl were most likely low (mean predicted value for $HCl_{(g)}$=0.03 $\mu g\,m^{-3}$), a consequence of having large excess of $NH_{3(g)}$ which tends to drive Cl^- into the aerosol.

Acknowledgements. C. Fountoukis and A. Nenes acknowledge NOAA (NMRAC000-5-04017) and the EPA (X83234201). AS and RW acknowledge NSF (ATM-0513035). T. VanReken acknowledges the NCAR Advanced Study Program. M. Fischer acknowledges the Laboratory

Directors Research and Development grant at the Lawrence Berkeley National Laboratory. E. Matías and M. Moya acknowledge CONACyT-J51782, PAPIIT-UNAM IN107306. Finally, D. Farmer and R. C. Cohen acknowledge NSF (ATM-0511829).

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Table 1. Comparison between predicted and observed concentrations of semivolatile species during the MILAGRO 2006 (21–30 March) campaign. Simulations are done assuming the aerosol can form solids ("stable" solution).

Data Type		$NH_{3(g)}$	$NH_{4(p)}$	$HNO_{3(g)}$	$NO_{3(p)}$	$HCl_{(g)}$	$Cl_{(p)}$
All data	mean observed ($\mu g\,m^{-3}$)	17.73±11.02	2.24±1.22	1.81±1.88	5.37±3.57	–	0.25±0.56
	mean predicted ($\mu g\,m^{-3}$)	16.89±10.97	3.08±1.56	1.38±1.92	5.80±3.86	0.03±0.11	0.22±0.55
	NME (%)	5.31	41.96	80.86	27.20	–	15.57
	NMB (%)	–4.70	37.14	-23.80	8.01	–	–15.57
CF=0	mean observed ($\mu g\,m^{-3}$)	17.33±9.83	2.37±1.18	2.63±1.87	5.57±3.50	–	0.28±0.56
	mean predicted ($\mu g\,m^{-3}$)	16.16±9.88	3.54±1.57	1.43±1.98	6.76±3.77	0.04±0.12	0.25±0.55
	NME (%)	7.16	52.30	71.72	33.87	–	17.56
	NMB (%)	–6.73	49.16	–45.49	21.49	–	–17.56
CF=1	mean observed ($\mu g\,m^{-3}$)	17.05±12.38	1.83±0.84	1.86±1.64	3.88±1.99	–	0.10±0.30
	mean predicted ($\mu g\,m^{-3}$)	16.49±12.23	2.39±1.07	1.73±2.32	4.00±2.36	0.01±0.05	0.09±0.29
	NME (%)	4.42	41.14	63.06	30.25	–	13.02
	NMB (%)	–3.26	30.38	-6.83	3.27	–	–13.02
CF=2	mean observed ($\mu g\,m^{-3}$)	16.63±8.27	2.54±1.71	0.00	7.31±4.89	–	0.28±0.33
	mean predicted ($\mu g\,m^{-3}$)	16.25±8.09	2.92±1.83	0.98±1.14	6.32±5.30	0.06±0.17	0.24±0.30
	NME (%)	2.96	19.39	–	13.46	–	23.91
	NMB (%)	–2.29	14.97	–	–13.46	–	–23.91
CF=3	mean observed ($\mu g\,m^{-3}$)	22.47±15.43	2.27±1.41	0.00	5.70±4.05	–	0.48±1.06
	mean predicted ($\mu g\,m^{-3}$)	21.99±15.16	2.74±1.64	0.73±1.05	4.96±4.03	0.02±0.06	0.46±1.05
	NME (%)	2.34	23.21	–	12.90	–	5.82
	NMB (%)	–2.12	21.02	–	–12.90	–	–5.82

Table 2. Effect of averaging timescale on ammonia, nitrate and chloride prediction error.

Averaging time	Error metric	$NH_{3(g)}$	$NH_{4(p)}$	$HNO_{3(g)}$	$NO_{3(p)}$	$Cl_{(p)}$
6 min (CF=0)	NME (%)	7.16	52.30	71.72	33.87	17.56
	NMB (%)	–6.73	49.16	–45.49	21.49	–17.56
20 min (CF=1)	NME (%)	4.42	41.14	63.06	30.25	13.02
	NMB (%)	–3.26	30.38	–6.83	3.27	–13.02
35min (CF=0)	NME (%)	6.68	49.48	64.15	30.54	19.58
	NMB (%)	–6.60	48.89	–51.17	24.36	–19.58

Table 3. Prediction skill metrics of ISORROPIA-II, for stable and metastable solutions. Data is shown for RH <50%.

Aerosol state		$NH_{3(g)}$	$NH_{4(p)}$	$HNO_{3(g)}$	$NO_{3(p)}$
Stable	NME (%)	3.56	24.32	67.67	25.83
	NMB (%)	–1.61	11.00	48.51	–18.52
Metastable	NME (%)	3.55	24.28	124.28	47.44
	NMB (%)	1.32	–9.03	121.61	–46.42

Table 4. Prediction skill metrics of ISORROPIA-II, for stable and metastable solutions. Data is shown for RH<50% and for sulfate-to-nitrate molar ratio larger and less than unity.

Solution Type	Error Metric	$NH_{3(g)}$	$NH_{4(p)}$	$HNO_{3(g)}$	$NO_{3(p)}$
		$SO_4^{2-}/NO_3^- > 1$			
Stable	NME (%)	4.85	38.68	28.83	41.45
	NMB (%)	0.59	–4.71	24.88	–35.77
Metastable	NME (%)	4.42	35.21	27.00	38.82
	NMB (%)	0.49	–3.95	23.04	–33.13
		$SO_4^{2-}/NO_3^- < 1$			
Stable	NME (%)	2.99	21.18	82.06	24.26
	NMB (%)	–2.07	14.71	56.18	–16.61
Metastable	NME (%)	3.08	21.84	159.02	47.02
	NMB (%)	1.08	–7.69	155.40	–45.95

Table 5. Sensitivity of volatile species to aerosol precursor concentrations.

Statistics		$NH_{3(g)}$	$NH_{4(p)}$	$HNO_{3(g)}$	$NO_{3(p)}$	$HCl_{(g)}$	$Cl_{(p)}$
	mean observed ($\mu g\,m^{-3}$)	17.73	2.24	1.81	5.37	–	0.25
	mean predicted ($\mu g\,m^{-3}$)	16.89	3.08	1.38	5.80	0.03	0.22
base case	NME (%)	5.31	41.96	80.86	27.20	–	15.57
	NMB (%)	–4.70	37.14	-23.80	8.01	–	–15.57
	mean predicted ($\mu g\,m^{-3}$)	16.57	3.40	1.40	5.78	0.03	0.22
	NME (%)	6.91	54.56	81.86	27.54	–	15.47
(+20%) TS	NMB (%)	–6.52	51.53	–22.52	7.58	–	–15.47
	Δx^* (%)	=–1.91	10.50	1.68	=–0.40	–=	0.12
	mean predicted ($\mu g\,m^{-3}$)	17.21	2.76	1.36	5.82	0.04	0.21
	NME (%)	3.99	31.50	79.87	26.87	–	15.70
(-20%) TS	NMB (%)	–2.91	22.95	–24.95	8.39	–	–15.70
	Δx^* (%)	1.88	–10.34	-1.50	-0.36	–	–0.15
	mean predicted ($\mu g\,m^{-3}$)	16.53	3.44	1.46	7.15	0.03	0.22
	NME (%)	7.11	56.20	83.92	41.06	–	15.32
(+20%) TN	NMB (%)	–6.75	53.36	–18.98	33.11	–	–15.32
	Δx^* (%)	–2.16	11.83	6.33	23.24	–	0.29
	mean predicted ($\mu g\,m^{-3}$)	17.25	2.72	1.26	4.48	0.04	0.21
	NME (%)	4.09	32.32	77.02	30.47	–	15.91
(-20%) TN	NMB (%)	–2.69	21.22	–30.06	–16.61	–	–15.91
	Δx^* (%)	2.11	–11.61	–8.22	–22.80	–	–0.40
	mean predicted ($\mu g\,m^{-3}$)	20.82	3.14	1.15	6.03	0.03	0.22
	NME (%)	17.62	43.29	75.36	25.35	–	14.76
(+20%) TA	NMB (%)	17.48	39.93	–36.47	12.27	–	–14.76
	Δx^* (%)	23.27	2.04	–16.63	3.95	–	0.96
	mean predicted ($\mu g\,m^{-3}$)	12.98	2.99	1.69	5.49	0.04	0.21
	NME (%)	26.74	40.26	88.89	29.91	–	16.79
(–20%) TA	NMB (%)	–26.74	33.29	–6.40	2.15	–	–16.79
	Δx^* (%)	–23.13	–2.80	22.83	–5.42	–	–1.45
	mean predicted ($\mu g\,m^{-3}$)	16.94	3.02	1.39	5.77	0.04	0.21
	NME (%)	5.09	40.27	80.44	27.06	–	15.96
(+20%) Na^+, Ca^{2+}, K^+, Mg^{2+}	NMB (%)	–4.42	34.97	–22.52	7.57	–	–15.96
	Δx^* (%)	0.29	–1.57	1.68	–0.40	–	–0.47

*Δx denotes the % change of the mean predicted value of each species compared to the base case prediction.

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Table 6. Effect of crustal treatment on predicted concentrations of ammonium, nitrate and water.

Property	Treatment of crustals	$NH_{4(p)}$	$NO_{3(p)}$	$H_2O_{(liq)}$
Mean Observed ($\mu g\ m^{-3}$)		2.24	5.37	–
Mean Predicted ($\mu g\ m^{-3}$)	Insoluble	3.18	5.47	13.23
	Equivalent Na	2.77	5.61	13.09
	ISORROPIA-II	2.55	5.86	11.67
NME (NMB), (%)	Insoluble	46.76 (41.53)	31.03 (1.87)	N/A
	Equivalent Na	34.3 (23.3)	28.7 (4.44)	N/A
	ISORROPIA-II	34.04 (13.6)	26.2 (9.2)	N/A

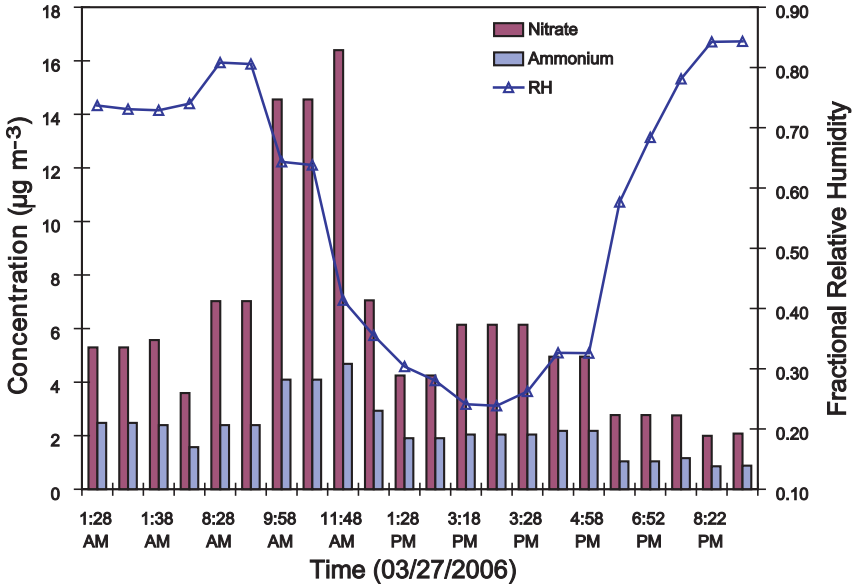

Fig. 1. Diurnal profile of measured nitrate, ammonium and ambient RH for 27 March 2006.

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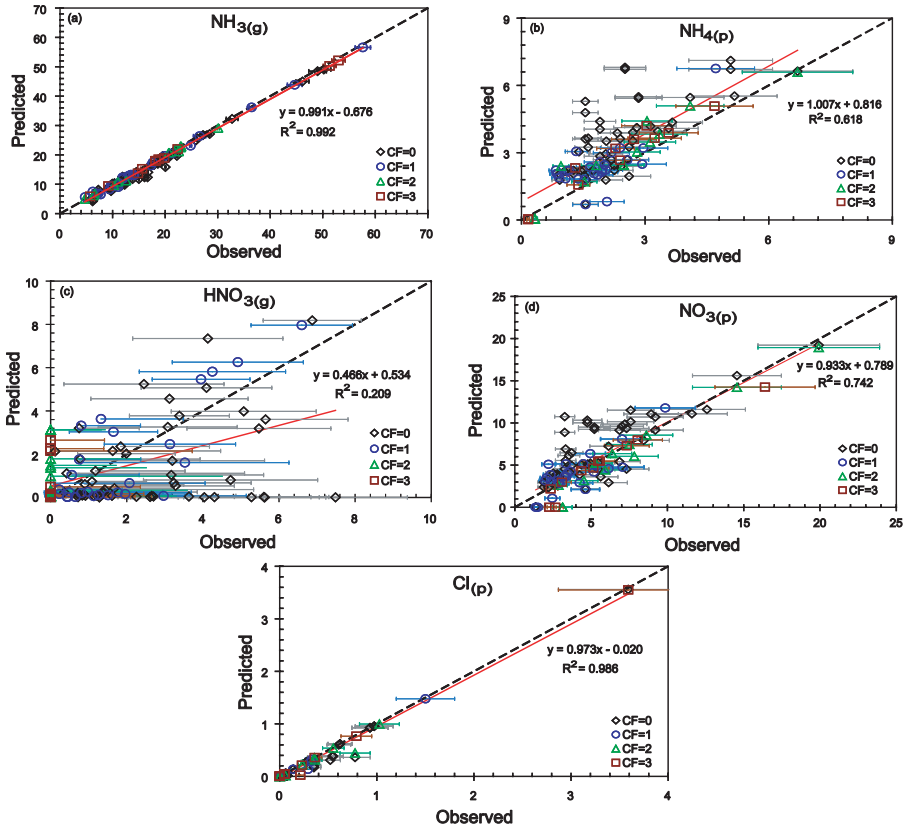

Fig. 2. Predicted versus observed concentrations ($\mu g\,m^{-3}$) of $NH_{3(g)}$ **(a)**, $NH_{4(p)}$ **(b)**, $HNO_{3(g)}$ **(c)**, $NO_{3(p)}$ **(d)**, and $Cl_{(p)}$ **(e)** during the MILAGRO 2006 (21–30 March) campaign. Description of legend is given in text. Linear regression line (for all data) is shown for reference. ISORROPIA-II was run assuming stable state solution.

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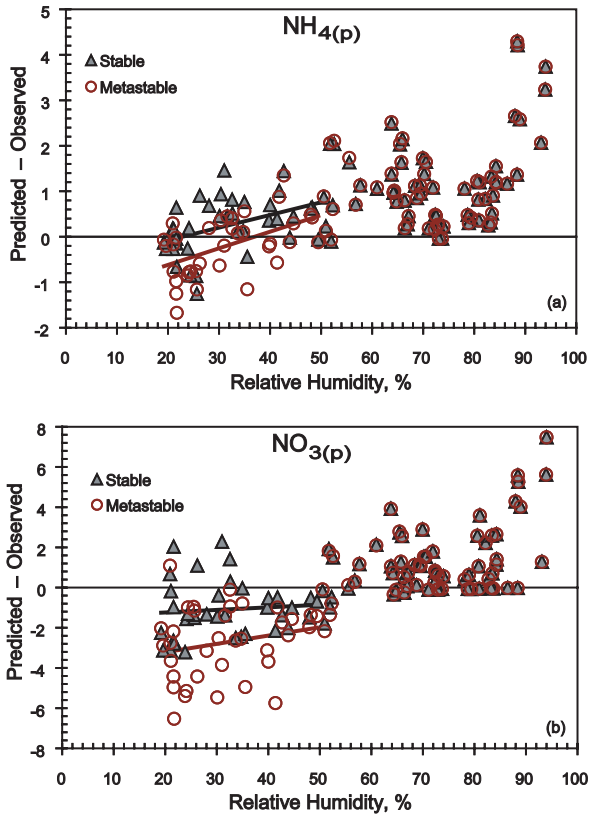

Fig. 3. Difference ($\mu g\, m^{-3}$) between predicted and observed concentrations of aerosol ammonium **(a)**, and, nitrate **(b)**, as a function of RH using the stable (deliquescence) and metastable (efflorescence) solutions of ISORROPIA-II. Linear regression lines are shown for both solutions at RH <50%.

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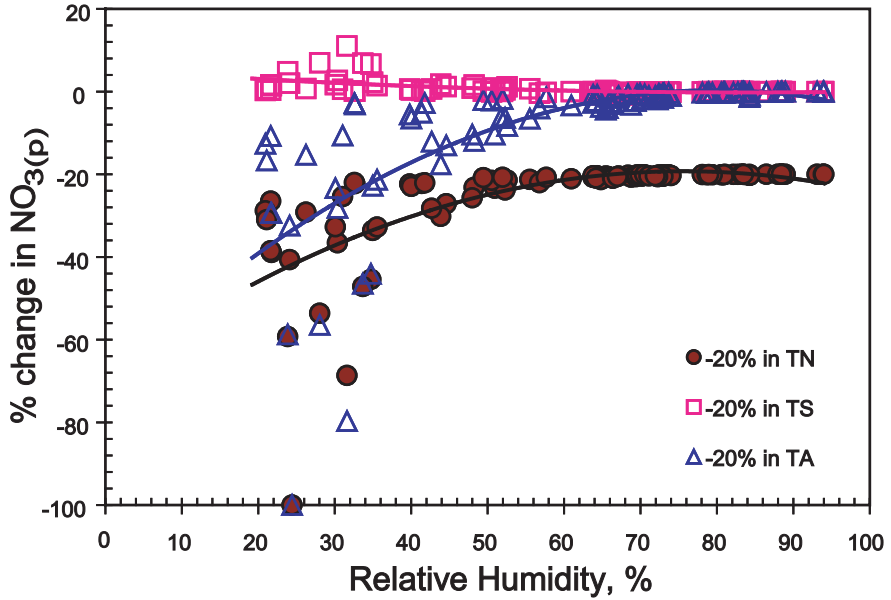

Fig. 4. Response of aerosol nitrate predictions of ISORROPIA-II (stable solution; forward mode) to a –20% change in TA, TS and TN as a function of RH. All data (CF=0–CF=3) are used in the dataset.

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